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Mobile Source NO_x Monitor

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An analyzer was developed for measuring motor vehicle NO_x (NO and NO_2) emissions based on the chemiluminescence reaction of NO and NO_2 with hydrogen atoms. This eliminated the need for an NO_2 to NO converter as required with ozone chemiluminescence for NO_x analysis. The hydrogen-atom source is based on the thermal dissociation of molecular hydrogen on a hot (~1900°C) tungsten filament. The unit has linear response to NO_x over a concentration range from 4 ppm to greater than 3000 ppm. No interferences were observed with H_2O, CO, CO_2, toluene, isopentane, NH_3, HCN, CH_3NH_2, or H_2 at concentrations encountered in raw automobile exhaust. Oxygen and ethylene caused minor interferences which should be inconsequential in actual application.

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MOBILE SOURCE NO_x MONITOR

HYDROGEN-ATOM DIRECT CHEMILUMINESCENCE METHOD

by

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ABSTRACT

Work was performed to determine the feasibility of using the H/NO chemiluminescent reaction as the basis for a mobile engine exhaust gas NO_X(= NO + NO_2) monitor which does not require a separate NO_2 to NO converter. This was followed by the construction and testing of a prototype instrument, the design of which is based on the findings of the feasibility study.

Following initial studies, a hot filament source was selected for H-atom production. In the (feasibility study) test flow reactor a linear response from 4 ppm to > 3000 ppm NO_X in N_2 was obtained, independent of the NO/NO_2 ratio. The test apparatus showed no interference by H_2O, CO, CO_2, C_2H_4, toluene, isopentane, NH_3, HCN, CH_3NH_2, or H_2 in the concentrations encountered in raw exhausts. Positive interference occurred with O_2; evidence was obtained that this interference is due to wall reactions and a wall-less reactor was therefore designed for the prototype instrument.

The use of the novel wall-less reactor made it necessary to perform extensive tests with the prototype and it was found necessary to obtain a tradeoff between sensitivity and negative and positive interferences occurring under these conditions. The performance of the prototype, as delivered, is: limit-of-sensitivity, 2 ppm NO_X; linear response, to > 3000 ppm NO_X; negative interference per 1% C_2H_4 and per 20% O_2 in the sample, 4% and 3% of NO_X signal, respectively; positive interference (in the absence of NO_X) at these same concentrations, 6 ppm equivalent NO_X, each. Graphs are provided herein, which indicate how these factors can be varied.

As discussed, performance, though adequate for mobile source monitoring, may be improved. Indications are that the H-atom direct chemiluminescence method could be made useful for ambient air NO_X monitoring conditions, where potential interferences are far less severe.

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SECTION 1

INTRODUCTION

Chemiluminescence monitors of NO_X (= NO + NO_2) are currently based on the NO/O_3 reaction.[1,2] To obtain NO_2 measurements this compound is converted to NO prior to entering the reactor. For mobile source exhaust observations thermal/catalytic converters are used for this purpose.[2,3] While these can perform satisfactorily for all diluted engine exhausts, errors can result with raw undiluted exhausts due to the reduction of NO_X to N_2. Additional errors can result from oxidation, in the converters, of other N-containing exhaust components (NH_3, HCN) to NO. To avoid such complications it is desirable to develop a method not requiring a separate converter. It was the goal of the work described herein to establish such a method based on the reactions

$$H + NO_2 \rightarrow NO + OH \quad (1)$$

$$H + NO + M \rightarrow HNO + M \quad (2)$$

$$H + NO \rightarrow HNO + h\nu \quad (3)$$

$$H + HNO \rightarrow H_2 + NO \quad (4)$$

The emission from Reaction (3) is a series of bands between 628 and 800 nm.[4-6] Reaction (3) leads to the expression for the chemiluminescence light intensity,

$$I \propto [H][NO] \quad (5)$$

Reaction (1) is a very fast process,[7,8] $k_1 = 3 \times 10^{10}$ ℓ mol^{-1} s^{-1}, and hence conversion of NO_2 to NO in the reactor is essentially instantaneous and the equation governing the monitoring method is thus

$$I \propto [H][NO_X] \quad (6)$$

The approach followed in this work was to first establish feasibility using a rack-mounted test apparatus (Sections 3 and 4) and then to build a prototype instrument and optimize its performance (Sections 5 and 6).

An alternative approach, which had been considered prior to initiation of this work, is the use of O atoms, based on the cycle

$$O + NO_2 \rightarrow NO + O_2 \quad (7)$$

$$O + NO + M \rightarrow NO_2 + M \quad (8)$$

$$O + NO \rightarrow NO_2 + h\nu \quad (9)$$

This approach has been used in two previous feasibility studies, i.e., those by Snyder and Wooten[9] and Black and Sigsby.[10] Snyder and Wooten's work was unsuccessful because the electrical discharge source used for O atoms itself produced fluctuating quantities of NO which resulted in apparently unsolvable background radiation problems. In the work of Black and Sigsby this problem was solved by using thermal decomposition of O_3 for the O-atom production. They obtained only a limited linear response range up to 50 ppm, inadequate for the high NO_x concentrations encountered in source monitoring. This appears to be due to the low O-atom concentrations achieved and the high reactivity of O atoms toward other species present in mobile source exhaust. By using small sample volume flow rates relative to the reagent flow rate it might, however, be possible to extend the use of their method to the higher [NO_x] (3000 ppm) needed for exhaust monitoring. Thus this approach appears to offer definite possibilities. However, though H-atom reaction kinetics has been less thoroughly explored than that of O atoms, H atoms are a priori more attractive since (i) the rate coefficients of reactions of H with hydrocarbons are typically an order of magnitude lower than those of O atoms (compare e.g., Refs. 8 and 11), (ii) H-atom chemiluminescent reactions are relatively rare (contrary to those of O atoms), thus reducing the number of potential interfering emissions, and (iii) [H] obtainable from thermal sources is of comparable magnitude to that from discharge sources.[12-14] Since H_2 is conveniently available free of O_2 and N_2, electrical discharge methods to produce H should not lead to the NO production problem encountered by Snyder and Wooten.

SECTION 2

OPERATING CONDITION RESTRAINTS

The high concentration of various compounds in raw exhausts places a priori restrictions on operating conditions. To evaluate these we had to consider the contractually required maximum concentrations of each of these compounds; these concentrations may be considered an upper limit to those anticipated to be encountered in raw exhausts. These are: NO_x (3000 ppm); H_2O (3%); O_2 (20%); hydrocarbons (1%), taken as ethylene, toluene, and isopentane; CO (7%); CO_2 (14%); nitrogen compounds (200 ppm), taken as NH_3, HCN, and CH_3NH_2; and H_2 (2%). Here the numbers in parentheses refer to volume concentrations in the sample gas to be considered. The maximum allowable combined interference* with the NO_x signal of all these compounds is 2%.

To determine the potential negative interference resulting from H-atom reactions, we took the reaction conditions used (Section 3.A) with the thermal source, i.e., P = 0.8 Torr, $\bar{v} = 7.6 \times 10^2$ cm s^{-1} and a reagent (H/H_2) to sample volume flow rate ratio of 100:1. We moreover took the portion of the reaction tube facing the center of the PMT as representative of what is being viewed by the whole PMT, which procedure, while not exact, certainly is valid for estimating the magnitude of interferences. Thus, since the distance of the sample inlet nozzle to the center of the 5 cm diam PMT is 4 cm, $t = 5 \times 10^{-3}$ s. The fastest bimolecular H-consumption reaction with a potential interferant* is that with ethylene, which has a rate coefficient (k) of 1×10^8 ℓ mol^{-1} s^{-1} at room temperature; for these conditions this would result in a decrease in [H] and hence in I, the chemiluminescence intensity, of 0.2%, which is negligible. The only other bimolecular H-atom reactions with the above interferants occurring at an appreciable rate are those with toluene and isopentane which, however, have a lower rate coefficient than ethylene.* Since total hydrocarbons can be assumed not to exceed 1% in the sample, the 0.2% consumption figure thus represents an upper limit. The NO_x itself will also consume H atoms. If we take all NO_x to be NO_2 (which is not realistic but again gives an upper limit) the H-consumption by Reaction (1) in the 100:1 diluted sample flow equals the total amount of NO_2 present, i.e., 3000 ppm $\times 10^{-2}$ = 30 ppm, which for 1% [H] in the reagent corresponds to an [H] loss of 0.3%.

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* Negative interference would result from H-atom consumption (cf., Eq. (6)) or emitter quenching, while positive interference would result from chemiluminescent reactions other than (3) which emit in the same wavelength region.

H-atom consumption also occurs via the catalyzed termolecular cycle represented by Reactions (2) and (4),* $k = 5 \times 10^{9}\ \ell^2\ mol^{-2}\ s^{-1}$.[8,15,16] The effective H-atom consumption k for the cycle is thus $2k_2 = 1 \times 10^{10}\ \ell^2\ mol^{-2}\ s^{-1}$, indicating an H-atom loss of 2.4×10^{-4}%. O_2 similarly catalyzes H-atom recombination via the reactions

$$H + O_2 + M \rightarrow HO_2 + M \qquad (10)$$

$$H + HO_2 \rightarrow H_2 + O_2 \qquad (11)$$

the effective k for which cycle is[17] $4.2 \times 10^{10}\ \ell^2\ mol^{-2}\ s^{-1}$ for $M = H_2$. Thus the H loss by this route is 8×10^{-2}%, again negligible but the dominant catalyzed H-atom loss process.†

These calculations, however, neglect the possible occurrence of emitter quenching by some of the potential interferants. Such negative interference could not be calculated a priori since no input data were available. The tests of Section 6 show the negative interference by quenching to be a restricting condition, but no more severe than the negative interferences by H-consumption.

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* The chemiluminescent Reaction (3), though phenomenologically written as a two-body process, is included in Reaction (2) and hence in k_2 expressions. Reaction (3) is thus actually a three-body process; however, the light emission is independent of [M] at the pressures of interest here, since the emitter quenching is also proportional to [M].[5]

† CO can also recombine H via a three-body process, $H + CO + M \rightarrow HCO + M$ followed by $H + HCO \rightarrow H_2 + CO$. These reactions, however, lead to negligible consumption since the governing rate coefficient[8] is $\approx 1 \times 10^{-3}\ k_{10}$ and [CO] is not anticipated to exceed 7% of the sample.

SECTION 3

FEASIBILITY STUDY - EXPERIMENTAL

A. Gas Handling System and Flow Conditions

The test apparatus is shown in Fig. 1. In the first part of the work H atoms were produced by a standard (e.g., Ref. 18) 2450 MHz microwave discharge in a 1.3 cm o.d. Vycor tube. The "reagent" H/H_2 from this source was found to cause interfering emissions when hydrocarbons were present in the sample. Later in the program therefore, the thermal H-atom source described further in Section 3.B was used. The other parts of the test apparatus were made of Pyrex, except for the valves, etc. and a copper tube coil between the sample feed and inlet systems used to reduce strain on the Pyrex. The 2.2 cm i.d. Pyrex reaction tube was poisoned with phosphoric acid to reduce H-atom wall recombination. For convenience Dri-Film SC-87 (a silicone product obtained from Pierce Chemical Co.) was used in the reagent feed lines. The Dri-Film, however, deteriorated rapidly in the reaction tube causing response variations and was therefore replaced with syrupy phosphoric acid. No wall poison was applied to the microwave discharge region or the thermal source. The "sample" NO_x was introduced from a 2ℓ exponential dilution flask, using ultrapure grade N_2 (dried by passage through activated alumina) as the diluent. The alternate inlet and bypass line, Fig. 1, were used for the high concentrations of NO_x required for spectrometric observations (Section 3.C) and also in selecting optimum flow conditions. The detector was a cooled ($\simeq -20°C$) tri-alkali PMT (Centronic P4283TIR); the light filter is discussed in Section 3.C. Three right angle bends ("tees") separated the microwave discharge and thermal H-atom source from the reaction tube. These bends served as light traps and successfully prevented light from these sources from producing a PMT response.

Sample volume flows 1% of the reagent flows were used, cf., Section 2. Optimum reagent flow conditions were established using an iterative procedure by throttling the pressure line at various reagent volume flows and observing the chemiluminescence intensities for NO volume flow $\simeq 2 \times 10^{-3}$ times the total reagent volume flow. Using the microwave discharge, we thus selected, except for a few preliminary experiments, a reaction zone pressure of 5.4 Torr at 13.2 $ml(STP)s^{-1}$ and an average gas velocity of 250 cm s^{-1}. For the thermal source 0.8 Torr at 6 $ml(STP)s^{-1}$ and an average gas velocity of 760 cm s^{-1} were used. The distance from the sample inlet to the viewing area of the PMT was 1.5 cm. Some background emission was always present in the absence of added NO; maximizing its intensity led to essentially the same optimum intensity conditions. In experiments with the microwave discharge it was found that 10% H_2 in He mixtures caused roughly a factor of 10 decrease in the background over that observed with undiluted H_2, essentially without affecting signal intensity.

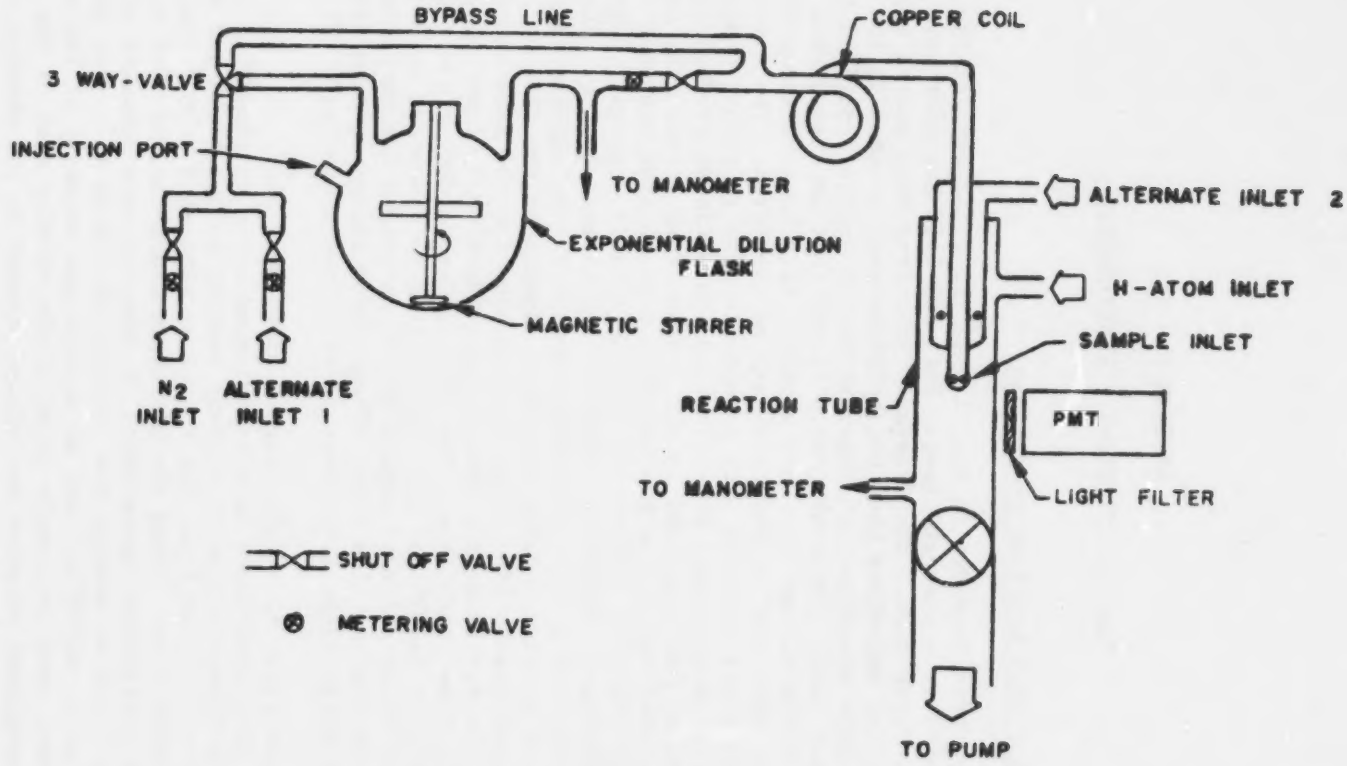

Figure 1. H/NO_x chemiluminescence analyzer test apparatus.

Such mixtures were therefore used. This point was not investigated for the thermal source and undiluted H_2 was used. The 10% H_2 in He mixture was pre-purified grade having an impurity content of 1 ppm $> [O_2] \geq 0.3$ ppm and "no" N_2, CO, CO_2. The undiluted H_2 was ultrahigh purity grade (min. purity 99.999%). Before passing through the H-atom generator these gases were purified further using a MG Scientific "Oxisorb" cartridge for reduction of O_2 to < 0.1 ppm and $H_2O < 0.5$ ppm.

The pressure in the exponential dilution flask was maintained at $\approx$ 11 Torr for the microwave discharge experiments and at $\approx$ 3 Torr in the experiments with the thermal H-atom source. Samples were injected into this flask using syringes. NO_2 is partially associated to N_2O_4 at atmospheric pressure and room temperature. The actual amount of NO_2 injected was calculated from the volume of the NO_2/N_2O_4 mixture, withdrawn as gas from the cylinder, using JANAF equilibrium data.[19]

To check for H_2O interference a room temperature saturator was used, as shown in Fig. 2. The volume flow through the saturator was 75% of the normal sample N_2 flow and entered the reactor through alternate inlet 2, Fig. 1, while the other 25% passed through the regular exponential dilution flask. Thus the total level of H_2O with which interference effects were checked was

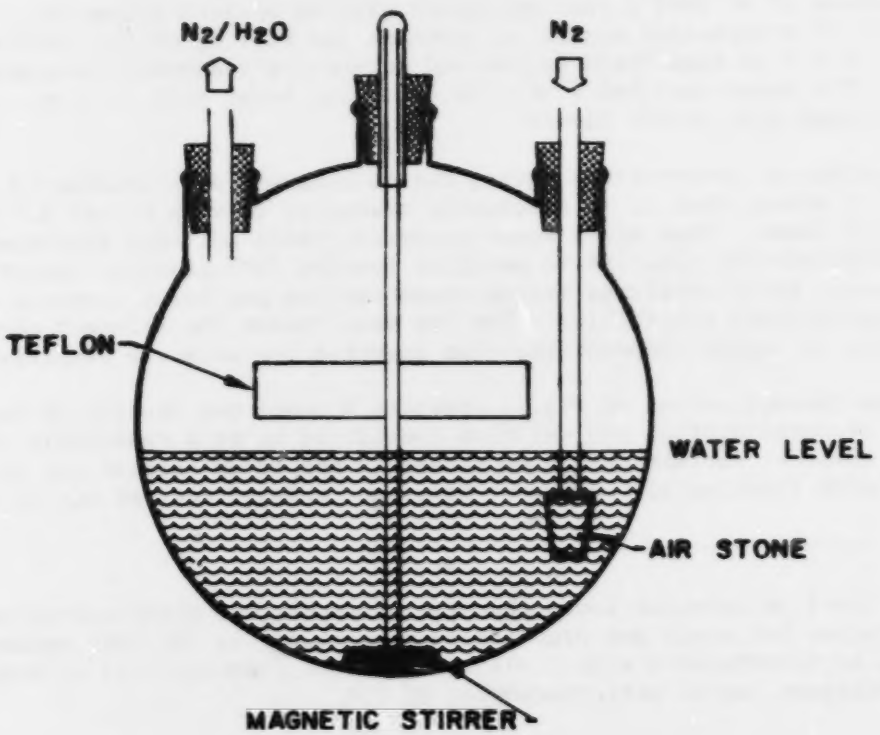

Figure 2. H_2O saturator.

2.25%.* Proper operation of the H_2O saturator was ascertained by trapping the H_2O in an activated alumina trap and weighing.

B. Thermal H-Atom Source

Hot tungsten filaments offer an attractive alternative to microwave discharges as H-atom sources. For a prototype instrument a thermal source offered the advantage of requiring only a simple power supply, thus eliminating the need to guard against electronic noise originating from the microwave power supply. Thermal sources described in the literature (e.g., Ref. 20) are water cooled, which did not appear practical for a prototype NO_x monitor. Thus the development of an air-cooled design was undertaken in the current program. Since the extensive testing of the lifetime and stability of such sources could not be done simultaneously with the investigations on the feasibility of the NO_x/H method (and at first appeared to represent an interesting but non-essential part of the feasibility study), this testing was done on a separate flow rig (available temporarily from work on another project) in which the thermal source was mounted just upstream from a microwave discharge cavity for ready comparisons; the reactor of this "test apparatus 2" was a 1ℓ stainless steel sphere coated with syrupy phosphoric acid.

Several designs were tested in the course of the program, with increasing success. The design ultimately incorporated in the main test apparatus, Fig. 1, for the final interference tests is shown in Fig. 3. With it dissociation was achieved with a 5 turn 0.025 cm diam W wire operated at 14 A, 33 V ac, at a temperature of ≈ 1900°C (as determined with an optical pyrometer). The filament was of ellipsoidal design to optimize the filling of the available space of the ≈ 7.5 cm diam Pyrex sphere and maintain a reasonable distance from its walls. The inner turn had a ≈ 2 cm diam, the outer ones ≈ 1 cm. Cooling was achieved with an air blower.

Incidental observations during the development work leading to the design of Fig. 3 showed that it is absolutely essential to keep O_2 and H_2O out of the H_2 supply lines. When minor leaks occurred, these not only shortened the filament lifetimes but also led to metallic looking (W?) deposits downstream from the source, which catalyzed H-atom recombination and hence severely affected [NO_x] measurement sensitivity. For the same reason the filament should not be heated to higher temperatures than required for adequate sensitivity.

The thermal source of Fig. 3 operated 8 hours per day for 40 days without a sign of deterioration and was thus considered to be a reasonably reliable tool. However, further design improvements had to be carried out in the prototype work (Section 5). The most important change required was to make a

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* This level is somewhat lower than the 3% requested, which corresponds to saturation but could not practically be achieved in the test apparatus. Since no interference with 2.25% was detected (Section 4.B) no significant interference can be anticipated for 3% H_2O.

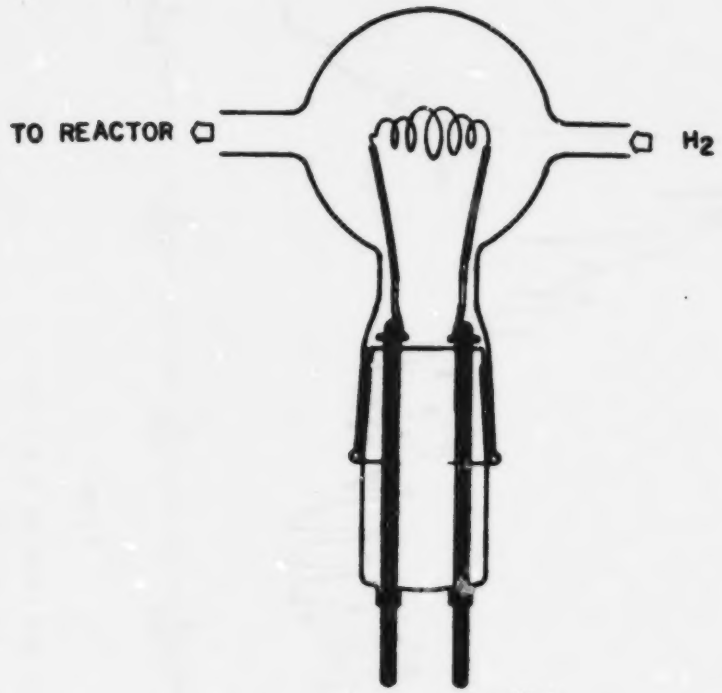

Figure 3. Thermal H-atom source.

permanently sealed source rather than one having a ground glass joint. The ground glass joint was essential for filament changing during source development work, but became an impediment for quantitative experiments on the main test apparatus, because of warming of the grease of the joint. The resulting vapors, though apparently not affecting the filament directly, led to a continuous decrease in sensitivity (increase in the ppm NO_x limit-of-sensitivity). Kel-F was found to be better in this respect than Apiezon-N.

C. Light Filter Selection

To aid in the selection of light filters for the PMT, spectra of the H/NO emission were taken, e.g. Fig. 4. It may be seen from these that maximum sensitivity can be anticipated by using $\lambda \geqq 660$ nm. The 762 nm peak is unsuitable since it is subject to interference by the peak intensity of O_2 ($^1\Sigma_g^+$) emission in the presence of O_2.[21,22] An available cut-off filter transparent to $\lambda \gtrsim 600$ nm* was the only light filter used for all experiments (Section 4), except those on O_2 interference for which additional filters were used as discussed in Section 4.B.

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* Little is gained by including the 600-660 nm region in which we found only very weak H/NO emission. The easy availability of the $\lambda \geq 600$ nm filter was the main reason for its selection.

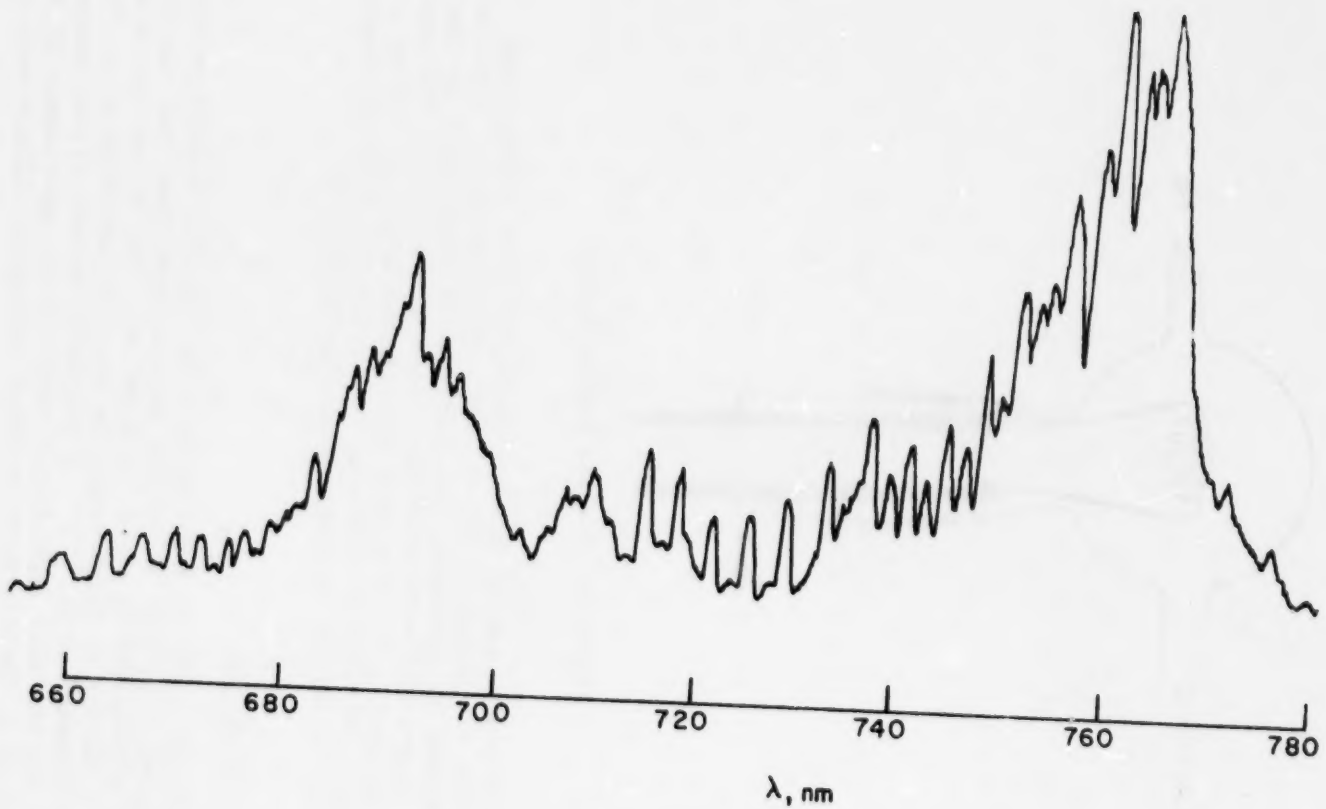

Figure 4. H/NO spectrum at 4.6 Torr.
H_2 = 2.1 x 10^{-4} mol ℓ^{-1}; NO = 3.2 x 10^{-5} mol ℓ^{-1}; $\bar{v}$ = 720 cm s^{-1}.
H atoms produced by a microwave discharge.

SECTION 4

FEASIBILITY STUDY - RESULTS

A. Linearity of Response and Limit-of-Sensitivity

Experiments were performed, using the microwave discharge source, to check the linearity of response for NO, NO_2, and 50% NO-50% NO_2 mixtures. Identical results were obtained, showing linear response from 2 to ≈ 3000 ppm NO_x. Hence the instrument response is independent of NO/NO_2 ratio. The limit-of-sensitivity here is taken as two times the smallest signal observable. A typical result is shown in Fig. 5. The solid line represents the average of a series of three NO tests made at an earlier date than the dashed line tests which pertain to the NO/NO_2 mixture. The magnitude of the deviations between the solid and dashed lines is comparable to that found in the individual NO runs from which the solid line was obtained and appears to represent injected sample size error and read-out uncertainty. Since the concentration coordinate is calculated for exponential dilutions, errors in pressure and flow rate readings will affect the slopes. For this reason the slope of the line drawn through the initial injection points (circles) is more reliable than those from the dilutions.

The limit-of-sensitivity indicated by these experiments is ≈ 4 ppm NO_x taken as twice the noise in the background signal. The best sensitivity achieved with the thermal H-atom source was also about 4 ppm. No attempts were made to generate plots like Fig. 5 with H from this source, mainly because of time/funding limitations and in view of the changes in response from the ground glass joint source used, as discussed in Section 3.B.

B. Interference Tests

These tests were made by adding the potential interferants at two extreme conditions: (i) with 3000 ppm NO_x injections and (ii) with no NO_x. The first tests optimized chances for synergistic effects, the second for discovering positive interference and influence on the background. Because of the potential for interference by the product OH of Reaction (1), NO_2 was used as the principal NO_x for each interferant. Frequent checks with NO yielded indistinguishable results. The interference gases checked and the concentrations and the H-atom source used are given in Table 1. For the gases checked at concentrations up to 200 ppm, co-injection with the NO_x samples was used. The larger concentrations used for the other interferants were obtained by substituting the gas injection for the required fraction of the N_2 dilution flask flow, using alternate inlet 1, and comparison to 100% N_2 flow through this flask.

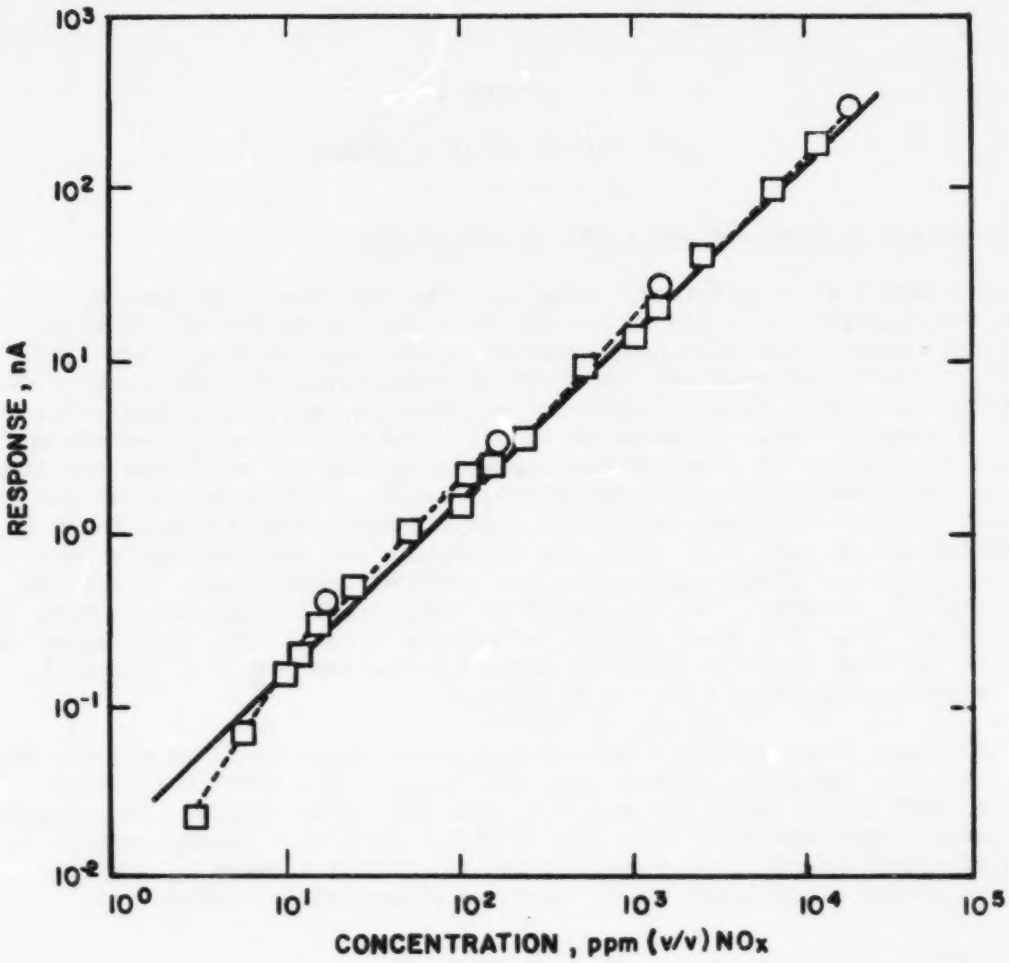

Figure 5. Response versus NO_x concentration.

——Average of three NO tests; - - -Individual injections of 50% NO-50% NO_2 mixtures; ○- initial injection points; □- points from exponential dilution.

TABLE 1. INTERFERENCE INVESTIGATIONS

Interferant	Concentration Tested	H-Source[a]	Interference Observed
H_2	2%	M	no
NH_3	200 ppm	M	no
CO	7%	M	no
CO_2	14%	M	no
HCN	300 ppm	M	no
C_2H_4	200 ppm	M	yes
	1%	T	no
Toluene	1%	T	no
Isopentane	1%	M	yes
	1%	T	no
CH_3NH_2	200 ppm	T	no
O_2	20%	T	yes
H_2O	2.3%	T	no

[a] M = microwave discharge. T = thermal source.

Isopentane and toluene were tested by producing a 10% mixture in N_2 in a stirred predilution flask. These samples were then co-injected with NO_x and compared to equivalent co-injected samples of pure N_2 and NO_x.

The first tests were performed with the microwave discharge. No interferences for H_2, NH_3, CO, CO_2, or HCN were found, i.e., in the presence of 3000 ppm NO_x the differences measured were well within the scatter of the data of a series of NO_x injections ($\lesssim$ 5%), while in the absence of NO_x, less than the equivalent signal of 2 ppm NO_x (in the background noise) was observed. However, using the microwave source, positive interference with ethylene and isopentane was observed. For either 200 ppm ethylene or 1% isopentane the interference in the absence of NO_x was the equivalent of 20 ppm NO_x and in the presence of 1000 ppm NO, the equivalent of 200 ppm NO_x; i.e., the total signal was then 1200 ppm NO_x. These hydrocarbon experiments were therefore repeated using the thermal source, which was also used for all further interference measurements. Using this source no interference with ethylene, toluene, isopentane, CH_3NH_2, or H_2O was observed. As discussed, the limit-of-sensitivity

varied depending upon the conditions of the thermal source and was, for the tests with C_2H_4 < 60 ppm, toluene < 6 ppm, isopentane < 20 ppm, CH_3NH_2 < 0.4 ppm,* and H_2O < 4 ppm NO_x equivalent. (Several days elapsed between the final tests on each of these compounds.)

Tests for O_2 interference were performed with a Ditric 7415SP "cut-on" filter (this filter has 42% transmission at 743 nm, 20% at 750 nm, and 1% at 760 nm, while the transmission from 600-730 nm $\geq$ 75%). It thus appears highly suitable for removing nearly all 762 nm O_2 radiation,[21,22] without affecting the bulk of the remainder of the HNO radiation. The second filter in these tests was a $\lambda \geq 680$ nm transmission cut-off filter. With this filter combination, 20% O_2 caused a positive interference (tested in the absence of added NO_x) equivalent to $\approx$ 800 ppm NO_x; the NO_x equivalent signal was linearly proportionally less for smaller $[O_2]$. This positive interference level was the same regardless of whether the O_2 was introduced through alternate inlet 1 or 2, i.e., through the center inlet in the reaction tube or the outer inlet 5 cm upstream from it, Fig. 1. This is clearly unacceptable.† The tests were therefore repeated using a Corion 692 nm, 13.4 nm FWHM interference filter without collimator.‡ This reduced the 20% O_2 signal to $\approx$ 300 ppm NO_x equivalent. Since some 760 nm radiation could still have been transmitted by this filter, it was then used in combination with a collimator (1 cm long with 0.3 cm diam holes) to remove any such radiation. This reduced the 20% O_2 level to $\approx$ 100 ppm NO_x equivalent. It can only be concluded that some O_2 emission occurs over the full wavelength region of H/NO emission. While Wayne et al[21] only discuss a peak at 762 nm, their Fig. 2 suggests that a weak tail of this emission extends down to at least 450 nm. We first assumed that a tail of such low relative intensity caused the observed interference.

To discriminate against this positive O_2 interference an approach similar to that used in the O/hydrocarbon chemiluminescence analyzer[18,23,24] was attempted, i.e., to subtract the output of two PMTs viewing the same section of the reaction tube at different wavelengths. These tests were carried out using the prototype hydrocarbon analyzer instrument[18] in which the O-atom source was replaced by the H-atom source of Fig. 3 and two Centronics 4283 PMTs were used. The Ditric 7415SP filter in combination with a Corning 2-64 filter was used for one of the PMTs. Through this filter combination the PMT thus viewed the

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* This figure was arrived at in a test with 20,000 ppm CH_3NH_2, 100 times higher than required, during which the NO_x limit-of-sensitivity was $\leq$ 40 ppm.

† These results pertain to thermal source experiments. Similar results were obtained using the microwave discharge.

‡ When no collimator is used, higher light intensities at the PMT cathode are achieved than when a collimator is used. However, without collimation, light enters the interference filter at angles other than the perpendicular incidence to which its nominal operation specifications apply, which results in some transmission at wavelengths other than those specified.

approximately 660-740 nm region. The other PMT, supplied with a Corning 7-79 filter, viewed the wavelength region from ≈ 750 nm to ≈ 800 nm, the approximate cut-off of the PMT. The reaction tube in this instrument was essentially the same as in the other H/NO_X tests described above and was coated with phosphoric acid. In these two-PMT tests a sample flow rate of 0.01 ml(STP)s^{-1} was used; the reagent flow rate was varied from ≈ 5-15 ml (STP)s^{-1} with a concomitant change in reactor pressure from 0.8 to 2.5 Torr. Both pure H_2 and 10% H_2 in He were used for the reagent flow. The results were unexpected, i.e., for O_2 as the sample gas both PMTs gave about the same response. Since the H/NO_X response by both PMTs was also approximately equal (2.3% NO_X in N_2 was used for the sample in this work), it was concluded that the two-PMT method was not useful here as it would require subtraction of signals of comparable magnitude.

The two-PMT tests nonetheless pointed the way to a solution of the problem in that they showed the H/O_2 signal to be unstable and poorly reproducible--changes on the order of 50% on various days were not uncommon--while the H/NO_X response was very stable and reproducible. Such behavior is typically what may be anticipated for heterogeneous (wall) reaction. The occurrence of such a process can also explain why the tail of the H/O_2 emission in this work is so intense relative to the peak at 762 nm. (Why a similarly intense continuum was not observed under the conditions of Wayne et al[21] still needs to be explained.) It was therefore decided to construct a "wall-less" reactor. This reactor was incorporated in the H/NO_X prototype instrument and is described in Section 5. The tests with the prototype instrument showed a decrease in the O_2/NO_X signal ratio by two orders of magnitude in the 690 nm region, cf. Section 6. This decrease reduces O_2 interference to acceptable levels and further confirms the H/O_2 wall chemiluminescence hypothesis.

SECTION 5

PROTOTYPE - DESCRIPTION

A schematic of the prototype NO_x analyzer is shown in Fig. 6. The element most different in principle from the test apparatus is the "wall-less" reactor, which will therefore be discussed first. It consists of two 2.2 cm i.d. lengths of reaction tubing separated by a ≈ 1 cm gap. These tubes are contained in a 1ℓ stainless steel sphere to provide vacuum. The upstream section of the reaction tube is constructed of Pyrex and has a side arm through which the H/H_2 enters the reactor, while the downstream tube is made of aluminum. The Pyrex tube is poisoned with phosphoric acid and is painted black on the outside. Sweeper gas can be added in the upstream section of the reactor. This gas flows out of the sphere through the gap between the reaction tubes and thus can be used to prevent the bulk of the reacting mixture from reaching the walls of the sphere. A 5 cm diam window on one side of the sphere permits viewing the gap, which thus represents the observed reaction zone. The bottom of the sample inlet nozzle is situated ≈ 0.5 cm upstream from this gap.

The general gas flow system, Fig. 6, is similar to that of the feasibility study. H_2 (ultrahigh purity or prepurified grade) flows through traps to remove O_2 (Englehard Deoxo catalytic hydrogen purifier) and H_2O (activated alumina). It is then partially dissociated in the thermal H-atom source. The thermal source used here was redesigned from that used in Section 3.B, mainly to eliminate the ground glass joint. The source, shown in Fig. 6, consists of a 20 cm long, 5 cm o.d. Pyrex envelope. The active element is a ≈ 10 cm long, 0.35 cm diam helical filament made of 0.025 cm diam tungsten wire. The filament, which has a resistance of ≈ 0.7 Ω, draws ≈ 8 A at 40 V. Relatively large size tubing (1.6 cm o.d. Pyrex) is used between this source and the reactor to minimize pressure drop. This connecting tubing is poisoned with phosphoric acid. A 10 CFM vacuum pump was used.

The trialkali PMT (Centronics P4283) views the reaction zone through two filters (Ditric 7415SP and Corning 2-60) with a combined bandpass from ≈ 640 to 740 nm. No collimator is used, which results in relatively large signal and background response. The advantage of this is that the dark current contribution to the background is negligible and hence, that no PMT cooling is required.

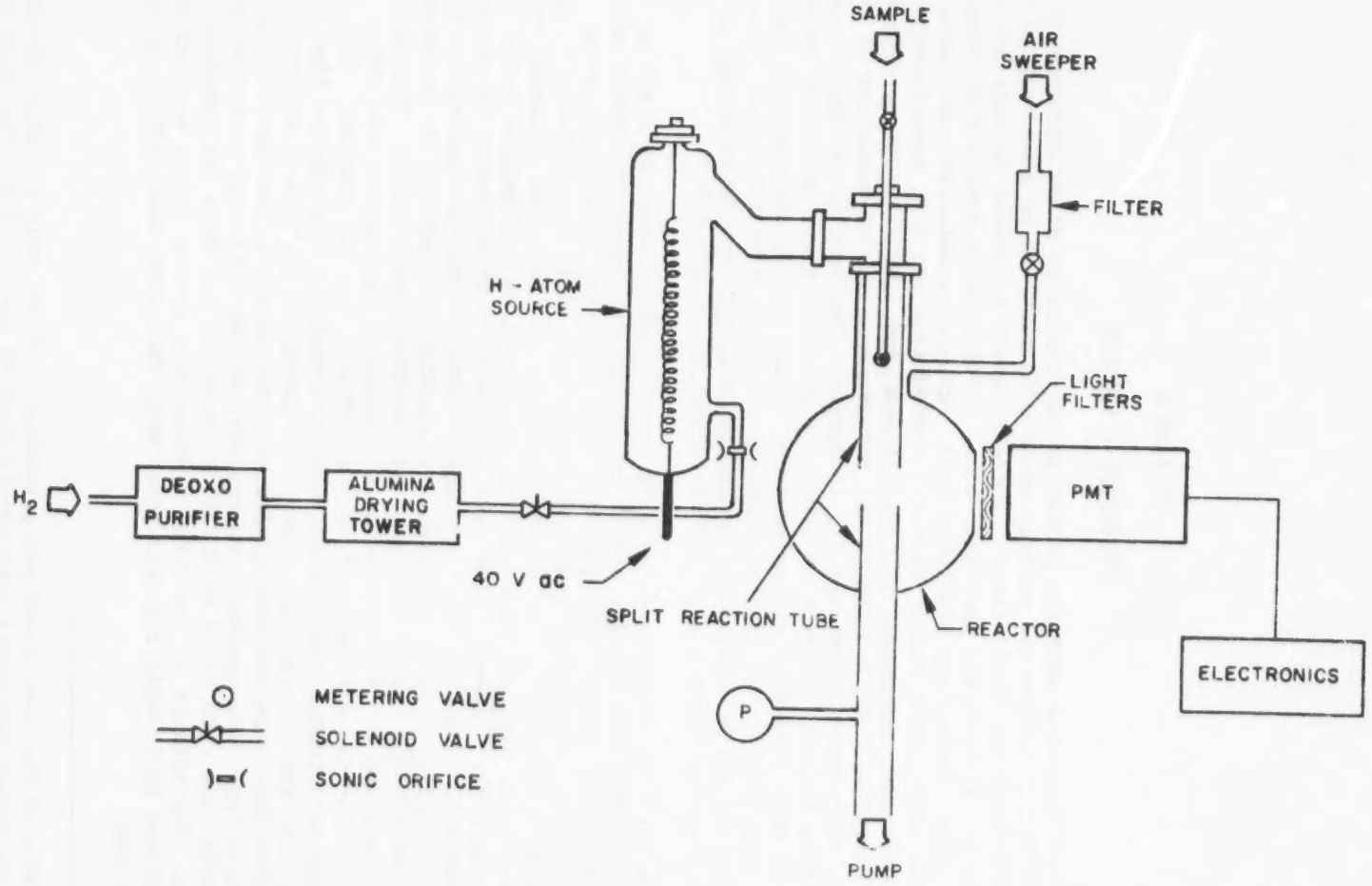

Figure 6. Schematic of prototype NO_x analyzer.

SECTION 6

PROTOTYPE - RESULTS

Tests were made with the prototype instrument to allow performance optimization and to define the various trade-offs that can be made between level of interference and sensitivity. While it would be useful to vary all parameters (e.g., flow rates, geometry, etc.) independently over a wide range of values, time limitations precluded this. Carefully selected tests were therefore made which dealt mainly with (i) positive O_2 and C_2H_4 interference due to chemiluminescent reactions, (ii) negative O_2 and C_2H_4 interference due to H-atom consumption, (iii) negative CO_2 interference due to quenching of the HNO emitter, (iv) sensitivity, and (v) linearity. The results of these tests make it possible for the operator of the instrument to choose operating conditions that best suit a particular application. Test results dealing with interferences, sensitivity, and linearity are presented in Sections 6.A-D. The final tests and the set of operating conditions selected for the delivered prototype (on the basis of these tests) are discussed in Section 6.E.*

The tests of Sections 6.A-D were carried out by choosing a set of "standard conditions" and varying one or two parameters while the others were at their "standard" value. The standard conditions for these tests were: sample flow rate, 2 $ml(STP)s^{-1}$; sweeper (air) flow rate, 0.4 $ml(STP)s^{-1}$; hydrogen flow rate, $\approx$ 18 $ml(STP)s^{-1}$; reactor pressure, 3.5 Torr; and filament voltage, 40 V at $\approx$ 8 A. Some of these choices were based on preliminary tests (e.g., the 0.4 $ml(STP)s^{-1}$ sweeper flow rate was found to be necessary to obtain linear response). However, the 2 $ml(STP)s^{-1}$ sample flow rate was chosen because it was initially thought that adequate sensitivity could not be achieved at the 0.1 $ml(STP)s^{-1}$ sample flow rate of the feasibility study. Therefore, the original aim was for a prototype instrument with two sample flow rates: 0.2 $ml(STP)s^{-1}$ for raw exhausts and $\approx$ 2 $ml(STP)s^{-1}$ for bag samples. Since lower flow rate performance can more reliably be predicted from higher flow rate results than can the reverse, tests were initiated with the 2 $ml(STP)s^{-1}$ rate. The higher than expected sensitivity that was achieved (Section 6.C) made the two sample flow rate approach unnecessary and the delivered prototype has only one sample flow rate (0.25 $ml(STP)s^{-1}$), suitable for both raw exhausts and bag samples. The effects of the three interferants tested (C_2H_4, O_2, and CO_2) were assumed to be additive--all tests were therefore made with N_2 as sample carrier gas.

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* The data of Sections 6.A-D are essentially of use only to those who might want to change the conditions established in Section 6.E. The more general reader may wish to proceed directly from here to Section 6.E.

A. Positive O_2 and C_2H_4 Interference

These tests were performed in the absence of NO_x. As concluded in Section 4.B the major outstanding positive interference problem to be investigated was that caused by O_2, i.e., the magnitude of its NO_x equivalent signal. Figure 7 shows that the response of the instrument toward O_2 with no sweeper flow is relatively large (30 ppm NO_x equivalent for 20% O_2) and nonlinear. When sweeper air is added, Fig. 8, the positive O_2 interference drops rapidly, while the response toward NO_x drops much more slowly*; hence, the positive O_2 interference in terms of NO_x equivalent signal is lowered. Because the background also rises as the sweeper flow is increased, the sensitivity drops more rapidly than the signal. The lowest possible sweeper flow rate should therefore be used. The 0.4 ml(STP)s^{-1} flow rate decided on for further tests is also sufficient to achieve linearity (see Section 6.D).

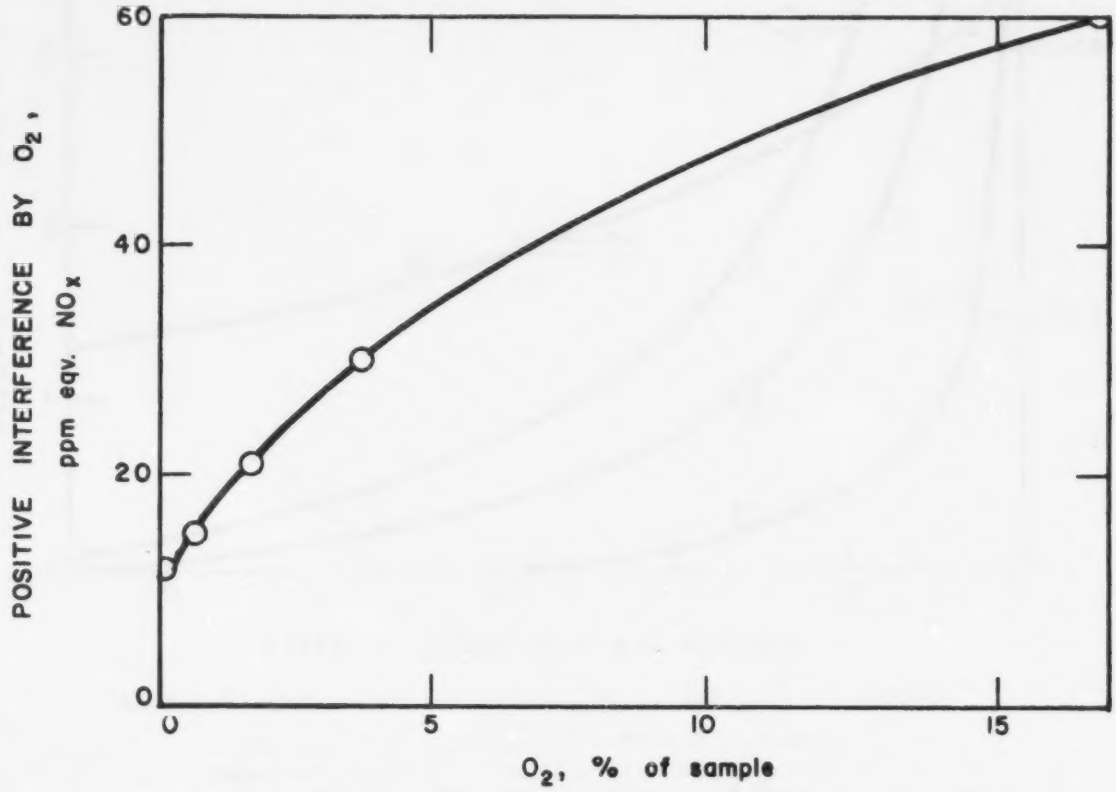

Figure 7. Positive interference by O_2 versus O_2 concentration in absence of sweeper gas.

Flows in ml(STP)s^{-1}: sample, 2.0, H_2, 18; reactor pressure, 3.5 Torr; filament voltage, 40 V.

* Under some conditions the opposite occurs (cf., Fig. 14).

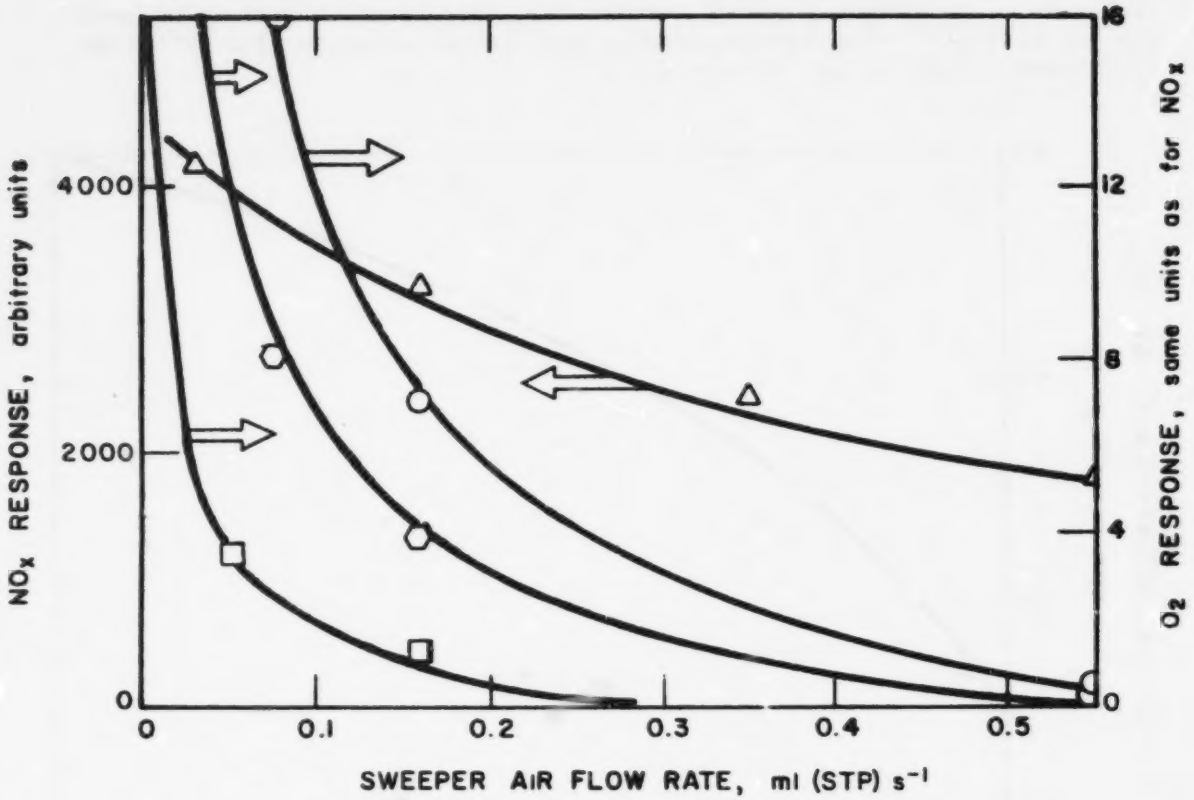

Figure 8. Response to NO_x and O_2 versus sweeper flow rate.

Flows in ml(STP)s^{-1}: sample, 2.0, H_2, 18; reactor pressure, 3.5 Torr; filament voltage, 40 V; △ - 4000 ppm NO_x, □ - 1.8% O_2, ⬡ - 3.6% O_2, ○ - 8% O_2.

The positive interference by C_2H_4 is smaller in magnitude than that by O_2 in the absence of sweeper air. A 1% C_2H_4 concentration results in about a 2 ppm NO_x equivalent interference, well below the level detectable in the experiments of Section 4.B. These results are shown in Fig. 9. The results of Section 4.B suggest that the largest positive hydrocarbon/amine interference would be expected for C_2H_4 and this 2 ppm NO_x level thus represents an upper limit for total positive hydrocarbon/amine interference.

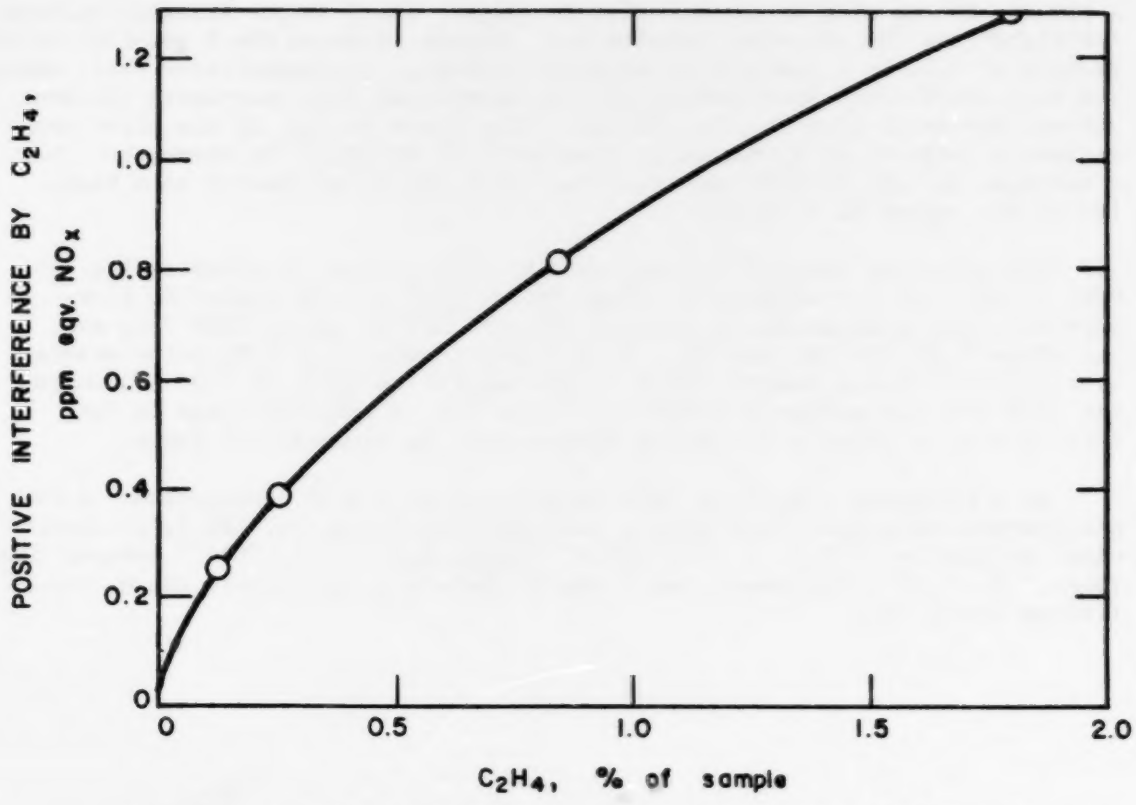

Figure 9. Positive interference by C_2H_4 versus C_2H_4 concentration.

Flows in ml(STP)s^{-1}: sample, 2.0, sweeper, 0.4, H_2, 18; reactor pressure, 3.5 Torr; filament voltage, 40 V.

B. Negative O_2, C_2H_4, and CO_2 Interference

While the feasibility work (Section 4.B) showed no negative interferences, operating conditions were, as noted, varied in the prototype work to obtain a trade-off between sensitivity and positive and negative interferences. Reaction time for the standard test conditions is roughly comparable to that for the feasibility work. However, the total pressure is higher and hence the partial pressure of the potential interfering reactants in the reaction mixture at the same dilution ratio is also increased. This necessitated some further evaluation of negative interference. C_2H_4 and O_2 were selected for these tests because of their potential interference by H consumption, cf. Section 2. CO_2, which at the 14% concentration level is the most probable interferant by quenching of HNO emission,* was tested in the work of Section 6.E only.

Since under our operating conditions [H] is in excess over $[C_2H_4]$, the absolute [H] consumed by this interferant, Δ[H], is independent of [H]. Therefore, the higher the [H], the smaller percentage interference to be expected. A priori, it can also be assumed that the higher the H-source filament voltage, the higher the [H], cf. also, Section 6.C. Figure 10 shows the % negative interference of C_2H_4 as a function of filament voltage. It demonstrates that, under the test conditions, interference by C_2H_4 occurs and that increasing filament voltage serves to minimize its effects. Also given in Fig. 10 are three measurements, made at an increased H_2 flow rate (30 ml(STP)s^{-1}); these show that a decrease in C_2H_4 interference results. This can be attributed to a higher [H] at the higher H_2 flow rate.

The effect of sample flow rate on C_2H_4 interference is shown in Fig. 11, both at 40 V and the standard H_2 flow, and at 50 V and the higher H_2 flow. As expected, the interference is roughly proportional to sample flow rate and therefore $[C_2H_4]$ in the reactor. A more direct measure of C_2H_4 interference as a function of its concentration in the reactor is shown in Fig. 12, where the $[C_2H_4]$ in the sample is varied from 0 to 1%. A small decrease in C_2H_4 interference is effected by adding sweeper gas, as shown in the figure.

O_2 also causes a negative interference due to H-atom consumption. A few measurements were made which showed that the interference by 20% O_2 is about equal to that by 1% C_2H_4 at 2 ml(STP)s^{-1} sample and 0.4 ml(STP)s^{-1} sweeper flow rates. The C_2H_4 interference tests should therefore approximate the O_2 interference fairly well.

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* Polyatomic molecules such as CO_2 are generally better quenchants than diatomic molecules such as O_2.

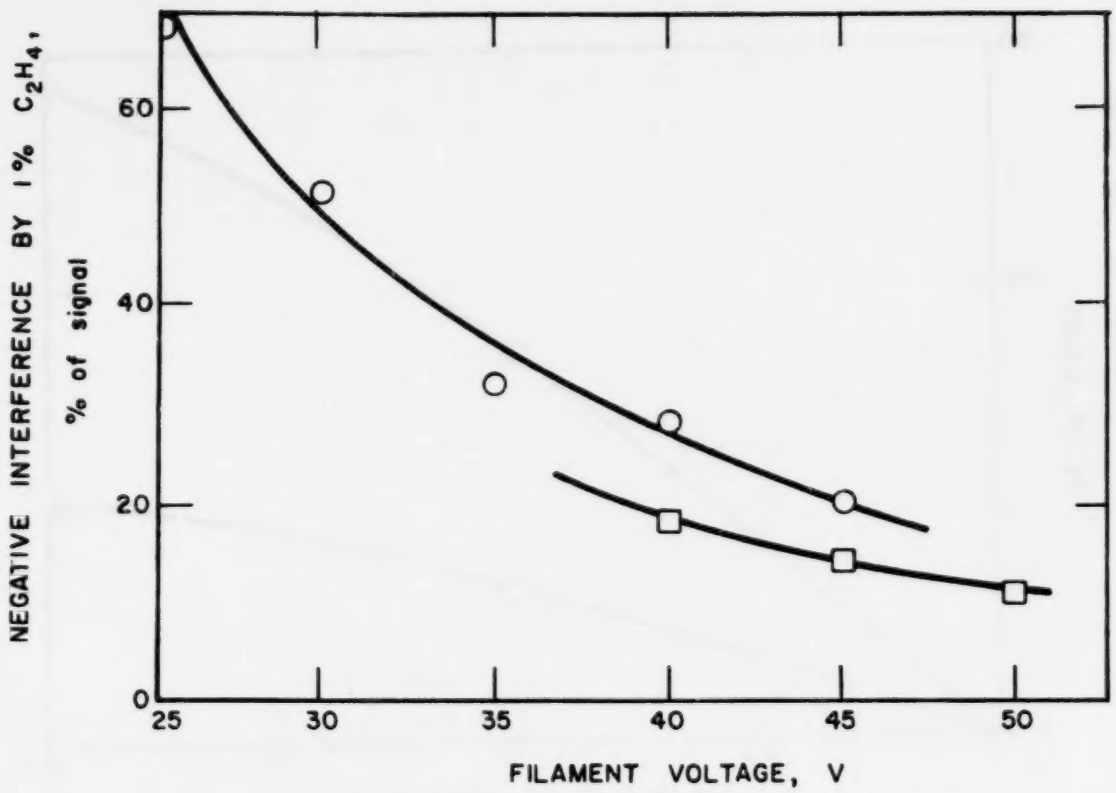

Figure 10. Negative C_2H_4 interference versus filament voltage.

Flows in ml(STP)s^{-1}: sample, 2.0, sweeper, 0.4, H_2, ○ - 18, □ - 30; reactor pressure, ○ - 3.5 Torr, □ - 6.0 Torr; filament voltage, ○ - 40 V, □ - 50 V.

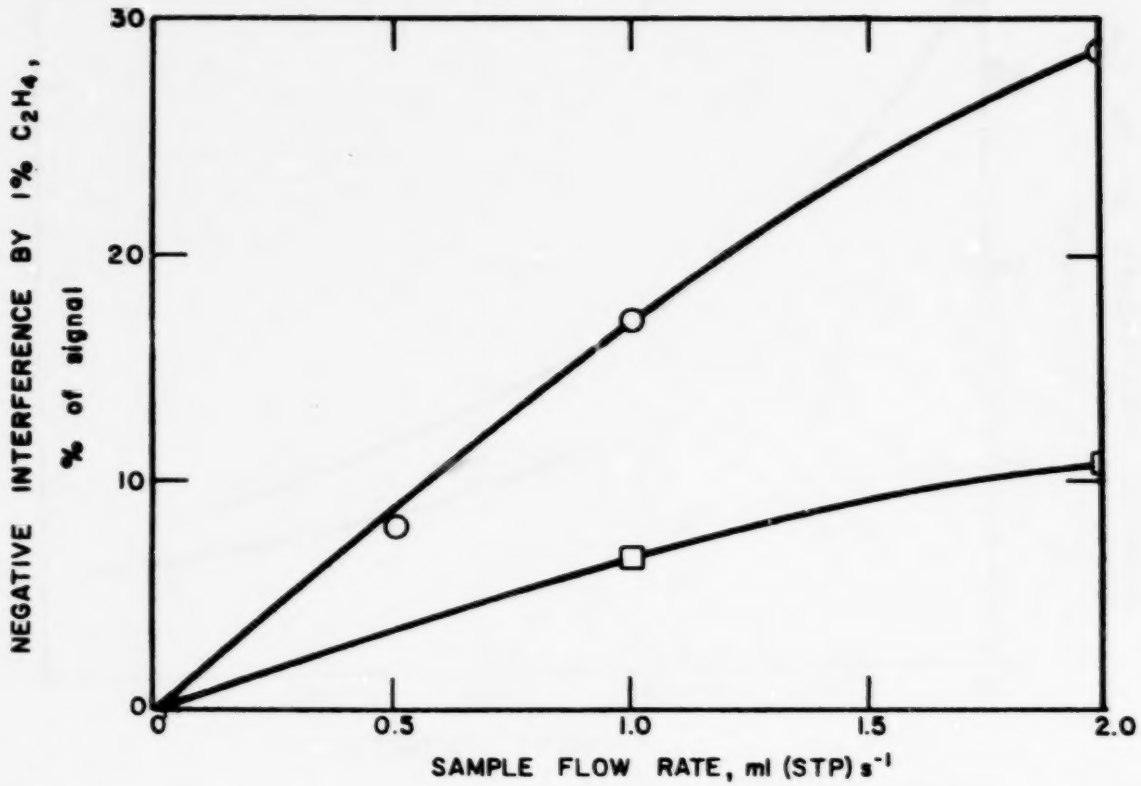

Figure 11. Negative C_2H_4 interference versus sample flow rate.

Flows in ml(STP)s^{-1}: sweeper, 0.4, H_2, ○ - 18, □ - 30;
reactor pressure, ○ - 3.5 Torr, □ - 6.0 Torr;
filament voltage, ○ - 40 V, □ - 50 V.

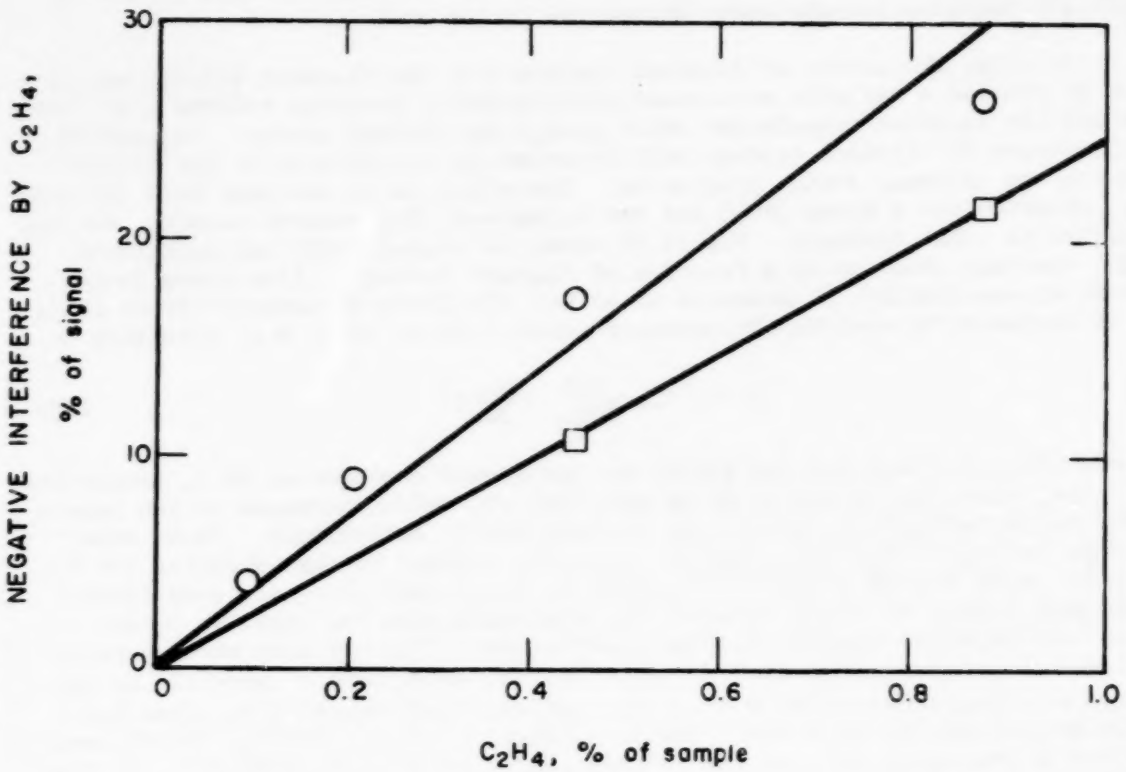

Figure 12. Negative C_2H_4 interference versus C_2H_4 concentration.

Flows in ml(STP)s^{-1}: sample, 2.0, sweeper, ○ - no flow, □ - 0.4, H_2, 18; reactor pressure, 3.5 Torr; filament voltage, 45 V.

C. Limit-of-Sensitivity

The parameters that most affect the sensitivity of the instrument are the H-source filament voltage and the sample flow rate (which control the [H] and the $[NO_x]$, respectively, in the reactor). A third parameter, which has a lesser influence, is the H_2 flow through the H source. It is more desirable to obtain a high sensitivity by increasing the filament voltage than by increasing the sample flow rate because the former will not cause an increase in the O_2 and C_2H_4 negative interference whereas the latter will.

To study the effect of filament temperature, the filament voltage was varied by placing a variable autotransformer between a constant voltage transformer and the stepdown transformer which powers the thermal source. In general, an increase in filament voltage will increase the temperature of the thermal source and increase H-atom production. The effect is to increase both the signal obtained for a given $[NO_x]$ and the background (for reasons unknown, but not related to light leakage). Figure 13 shows the signal (SIG) and background (BG) readings obtained as a function of filament voltage. Also shown is the limit-of-sensitivity, S, measured at 40 V.* The limit-of-sensitivity at other V is estimated by scaling the measured sensitivity at 40 V, S_{40}, according to

$$S = S_{40} \frac{SIG}{SIG_{40}} \left(\frac{BG_{40}}{BG}\right)^2 \qquad (12)$$

where SIG_{40} and BG_{40} are the signal and background measured at 40 V, respectively. For this calculation it is assumed that the noise increases as the square root of the background and reduces the sensitivity accordingly. Thus, even though the signal increases rapidly up to the highest voltage measured (50 V), little can be gained above 50 V because the background increases even faster. Some gain beyond 50 V may, however, be obtainable when the negative O_2 and C_2H_4 interferences (Section 6.B) are considered. This may come about because a lower interference at a high filament voltage would make it possible to operate at a higher sample flow rate for a given interference level, when the filament voltage is increased. However, beyond a certain voltage the filament begins to evaporate and coat the thermal source walls with tungsten.† At that point the sensitivity decreases sharply due to H-atom recombination on the source walls, cf., Section 3.B.

The H_2 flow rate through the thermal source has a relatively small effect on response. Under the standard conditions, an increase of H_2 flow to 30 $ml(STP)s^{-1}$ results in a $\approx$ 20% increase in signal.

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* The limit-of-sensitivity was taken to be twice the short term peak-to-peak noise level in ppm equivalent NO_x obtained with room air as sample.

† Such a destructive test was attempted using a similar H-atom source as that used in the above tests but with a different filament. In that earlier test a decrease in signal ultimately resulted from an increase in filament voltage. It is estimated that the voltage at which the signal begins to decrease would be $\approx$ 65 V for the filament used in the present tests.

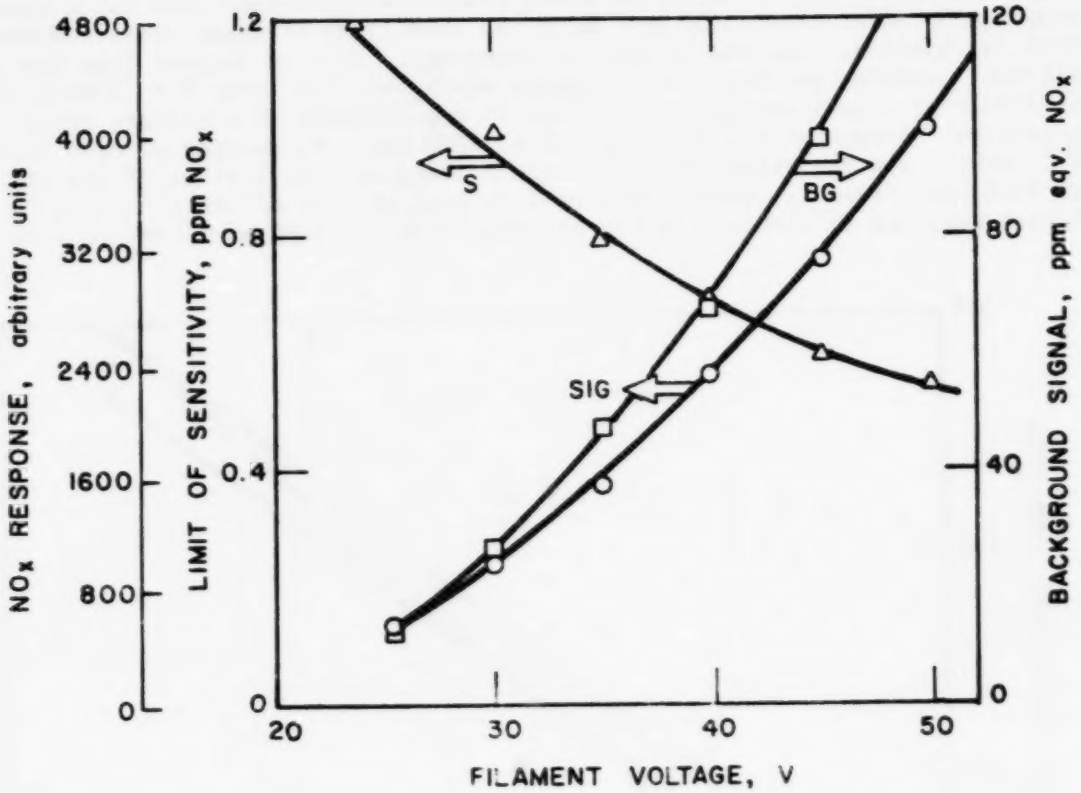

Figure 13. Response to 4000 ppm NO_x and limit-of-sensitivity (left ordinate) and background signal (right ordinate) versus filament voltage.

Flows in ml(STP)s^{-1}: sample, 2.0, sweeper, 0.4, H_2, 18; reactor pressure, 3.5 Torr.

D. Linearity

Linearity tests were carried out using a 5000 ppm NO_2 in N_2 sample, diluted progressively further with N_2. Measurements were made by comparing readings from the H/NO_X instrument to those of an AeroChem built $NO/NO_X/O_3$ analyzer modified to measure high $[NO_X]$ (up to 1%). Many previous tests on these modified instruments have shown them to be linear to well past the 1% level. As the measurements of Fig. 14 show, the H/NO_X prototype instrument also has a linear response up to at least 5000 ppm under the conditions of these tests. Sweeper flow is, however, required to achieve linearity. With no sweeper flow the instrument response was found to be highly nonlinear; the ratio $R = (H/NO_X)$ signal/(O_3/NO_X) signal varied from 0.77 at 40 ppm (signals in arbitrary units but consistent throughout the test) to 2.0 at 5000 ppm. N_2 sweeper at 0.09 ml(STP) s^{-1} reduced the deviation, Fig. 14, with R changing from 1.46 at 35 ppm to 1.82 at 5000 ppm. Finally, with a sweeper flow rate of 0.36 ml(STP)s^{-1} of N_2, a linear response to within ± 4% was obtained from the 1.09 at 17 ppm to 1.00 at

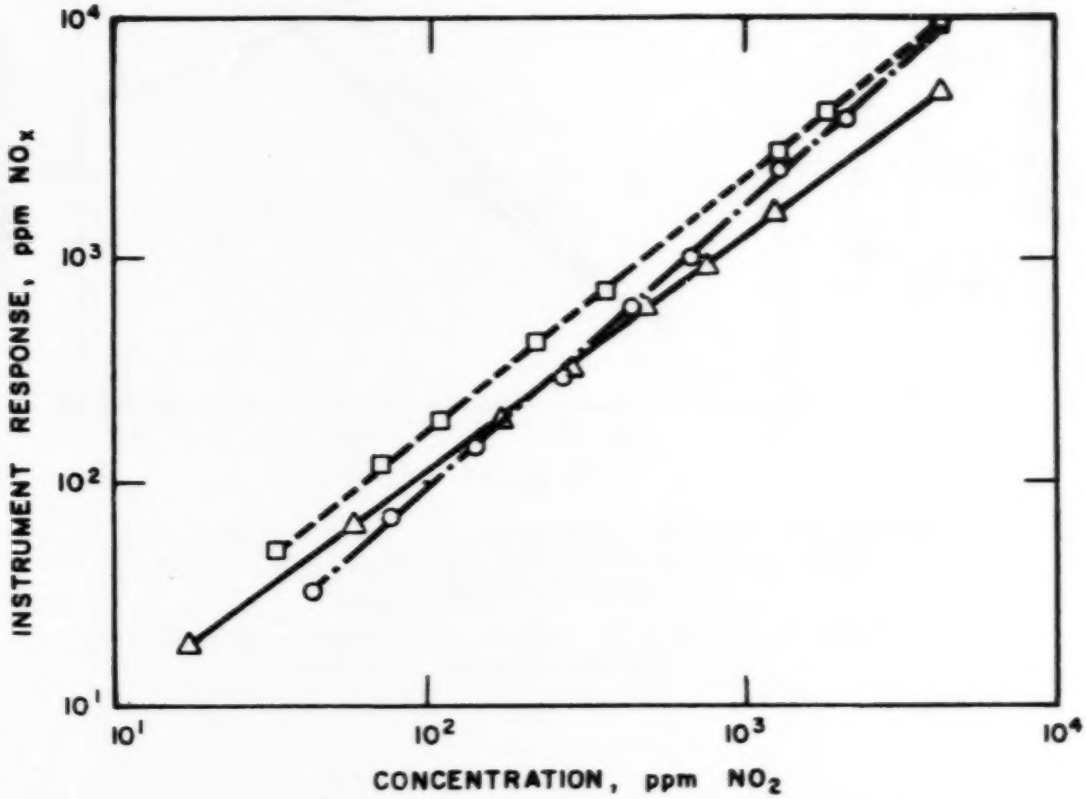

Figure 14. Response versus concentration of NO_2.

Flows in ml(STP)s^{-1}: sample, 2.0, H_2, 18, sweeper, ○ —·—·— none, □ – – – 0.09, △ ——— 0.36; reactor pressure, 3.5 Torr; filament voltage, 40 V.

5000 ppm. The reason for the nonlinearity at low sweeper flow rates is probably the flow disturbance caused by the gap in the split reaction tube.

E. Selection of Operating Conditions

From the tests discussed in Sections 6.A-D, tentative operating conditions were selected for a reasonable compromise between sensitivity and interferences, as follows: 0.4 ml(STP)s^{-1} sample and sweeper flow rates; 18 ml(STP)s^{-1} H_2 flow rate; 3.5 Torr reactor pressure; 45 V filament voltage at 10 A; and a separation of 0.5 cm between the tip of the sample inlet nozzle and the downstream end of the upper reaction tube. However, prior to final testing, the instrument was cleaned and carefully re-assembled. Measurements with the instrument thus improved showed the response towards NO_x as well as the background to be much larger than before the cleaning, the negative C_2H_4 interference to be absent, and the positive C_2H_4 interference to be very large ($\approx$ 100 ppm equivalent NO_x).* These results can be attributed to a much larger [H]† than was obtained prior to this overhaul.‡ To minimize the positive C_2H_4 interference a number of changes in operating conditions were made, the most important of which was to increase the distance between the tip of the sample inlet nozzle and the observation region to 8 cm. This change reduces the positive interference by C_2H_4 by reactively removing this compound.§ A decrease in response to C_2H_4 can also be effected by reducing [H]; the filament voltage therefore was reduced (to 40 V). The larger H-atom consumption by both C_2H_4 and O_2, thus resulting from the longer reaction distance and hence time, inevitably manifested itself in increased negative C_2H_4 and O_2 interference.

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* It is probable that a behavior of the instrument very similar to that obtained in the tests of Sections 6.A-D can be re-obtained by a major decrease in filament voltage, and thus in the [H], to the levels of those tests.

† Titration[8] of H atoms with a 0.5% NO_2 in N_2 sample at a 14 V filament voltage showed the $[H]/[H_2]$ to be $\approx 4 \times 10^{-4}$. The instrument response to NO_x at 50 V is $\approx$ 500 times larger than at 14 V which implies a $[H]/[H_2] = 0.2$ at 50 V (at 12 ml(STP)s^{-1} H_2).

‡ The large positive C_2H_4 interference, reported in Section 4.B for experiments with the microwave discharge H-atom source, can also be attributed to high [H] obtained with that source.

§ At 40 V, 0.3 ml(STP)s^{-1} sample flow, and 0.2 ml(STP)s^{-1} sweeper flow, the positive interference by 1% C_2H_4 dropped from 12 ppm NO_x equivalent at a nozzle-to-observation zone distance of 3 cm to 8 ppm at 5 cm and 4 ppm at 8 cm.

This interference was therefore reduced by decreasing the sample flow rate to 0.25 ml(STP)s^{-1}, which was found to provide a reasonable compromise between negative interference levels and sensitivity.

The operating conditions finally used in the delivered prototype instrument are: sample flow rate, 0.25 ml(STP)s^{-1}; sweeper flow rate, 0.4 ml(STP)s^{-1}; H_2 flow rate, 12 ml(STP)s^{-1}; filament voltage and current, 40 V and 8 A; reactor pressure, 2.5 Torr; sample nozzle-to-observation zone distance, 8 cm. Under these conditions the performance of the instrument (again for N_2 sample gas) is the following: limit-of-sensitivity 2 ppm NO_x with a 3 s electronic time constant and 6 ppm NO_x for a 0.3 s time constant; positive interferences for 1% C_2H_4 and 20% O_2 6 ppm equivalent NO_x each; negative interferences for the same quantities of C_2H_4 and O_2, 4 and 3%, respectively; negative interference for 14% CO_2, less than 3%. The response of the instrument has been found to be linear to within ± 2% from 6 ppm to at least 3000 ppm NO_2. Comparison to the work of Section 6.D suggests that linearity would be retained to at least eight times the limit investigated there, i.e., to 4% NO_x. This is so since an eight times smaller sample flow rate is used here than that of Section 6.D, and the H consumption by NO_2 is the factor determining the upper limit. Because NO_x concentrations higher than 3000 ppm are not of practical interest, this point was not re-investigated.

SECTION 7

DISCUSSION AND PROJECTIONS

While the operating conditions arrived at from the tests have resulted in a prototype instrument that is adequate for mobile source monitoring requirements, improvements can be made that will result in improved sensitivity (for a given interference level) or lower interferences (for a given limit-of-sensitivity). Investigation of such changes was outside the time and funding scope of this contract but it would appear useful to summarize pertinent ideas here. Additionally, it may be possible to improve sensitivity to the point that an H/NO_x instrument would be useful for ambient air measurements. For this latter application trade-offs should be made that would favor sensitivity at the expense of interferences. This is possible since of the two major interferants encountered in the present work, one, O_2, is present at a constant concentration in ambient air and the other, hydrocarbons, at a much lower concentration than encountered in mobile source monitoring ($\leq$ 10 ppm as compared to 10^4 ppm). Projections can thus be divided into two categories: (i) general improvements and (ii) ambient monitoring.

General Improvements

1. The optical filter could be replaced with a wider bandpass filter since homogeneous gas-phase emissions at 762 nm appear unlikely to add much to positive O_2 interference, which problem has been solved in the prototype instrument.

2. A PMT with higher sensitivity than the P-4283 used in the 650 to 800 nm wavelength region would lead to increased sensitivity.

3. A larger diameter reaction tube would result in more signal. Optimizing the present reactor should provide a more intense signal as well, e.g., the reaction zone to PMT cathode distance could be decreased.

4. An investigation of the nature of the background radiation could lead to means for its reduction, which would result in increased sensitivity. Use of a supersonic jet reaction zone might eliminate the background altogether.

Ambient Monitoring

5. Sample flow rates comparable to the $H_2/(Ar, He)$ could be used, probably resulting in an order of magnitude improvement in limit-of-sensitivity. While this would result in an increased H consumption by O_2, such consumption would be constant and therefore not of overriding importance.

6. Since the variation in [H] decrease, i.e., negative interference due to reaction with O_2 and hydrocarbons, would essentially be eliminated, the observation zone could be extended to include all or most of the reaction zone. Thus use of an integrating sphere or spiral reactor might lead to an order of magnitude improvement.

7. Increasing [H] in the observed reaction zone would result in a proportional increase in light intensity, cf. Eq. (5). Moreover, such an increase in [H] would allow higher sample flows (since negative interferences are reduced) leading to further signal increases. The positive ethylene interference resulting from a high [H] could be reduced by mixing the H/H_2 and sample flows well upstream of the PMT viewing area (cf., Section 6.E). A number of means for increasing [H] appear available: (i) operating at a higher filament voltage than used in the present instrument, (ii) further improvements in the thermal source design, and (iii) reconsidering the use of an electrical discharge method for H production.

8. Combination of items 5-7 with the suggested general improvements, items 1-4, may result in a limit-of-sensitivity in the 1-10 ppb range required for ambient monitoring. It is clear that the interaction of the possible changes would have to be investigated in such a context.

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